

# PATENT ABSTRACTS OF JAPAN

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## (54) TREATMENT OF SURFACE OF STAINLESS STEEL

(57)Abstract:

**PROBLEM TO BE SOLVED:** To increase affinity and the thermal conductivity of a stainless steel to vapor or liquid to promote its dispersion and evaporation in the case liquid is brought into contact therewith and to improve coating adhesion thereof by immersing a stainless steel in an iron oxide ion and chromium oxide ion-contg. treating soln. prepd. by specified treatment and forming iron oxide coating film thereon.

**SOLUTION:** A stainless steel immersed in an iron oxide ion ( $\text{FeO}_4^{2-}$ ) and chromium oxide ion-contg. treating soln. obtd. by executing electrolytic treatment with a chromium-iron alloy as the anode in an alkali aq. soln. to form iron oxide coating on the surface. As the chromium-iron alloy to be used as the anode, a ferritic stainless steel contg., by weight, about 0.12% C and about 12 to 25% Cr or a martensitic stainless steel contg. about 0.10 to 1.00% C and about 11 to 17% Cr is suitable. As for the cathode material, limitation is not particularly placed, and the one same as the anode material, the other alkali resistant conductive material or the like may be used.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention gives the compatibility over a steam or a fluid to the surface of a stainless steel material, and relates to the new surface treatment method of a stainless steel material for both raising heat-conducting characteristic, film adhesion, and corrosion resistance as if the distribution at the time of contacting a fluid and evaporation being promoted.

[0002]

[Description of the Prior Art]Stainless steel is steel which uses chromium as main alloy elements, and five sorts, austenite, a ferrite series, an austenite ferrite series, a martensite system, and a precipitation-hardening system, are known. Since it excels in corrosion resistance, heat resistance, chemical resistance, surface brightness and gloss, water repellence, etc., in many fields, these stainless steel materials are used broadly.

[0003]However, since this stainless steel material has high water repellence, a uniform liquid thin film is hard to be formed in that surface, When heat-conducting characteristic was checked as a result, and the efficiency of the mass transfer in the case of steamy condensation operation or evaporation operation of a fluid and heat transfer is low and also it paints, it has a fault, like the adhesion of a coat is small.

[0004]By the electrochemical reaction through the solid in which the stainless steel material adhered to the surface, or a drop. The corrosion-resistant characteristic which is easy to receive corrosion and a stainless steel material has as a result is spoiled, For example, advance etc. of spot corrosion with the high concentration nitric acid system and sulfuric acid system liquid which are generated by advance of the corrosion of the stainless steel material in a coastal area with much brine injury or repetition of the waterdrop formation, and the evaporation and condensation by the exhaust gas in a highway tunnel pose a problem.

[0005]In order to improve the fault which such a stainless steel material has, to give lyophilicity, for example on the surface of a stainless steel material, to make a liquid thin film form without spoiling corrosion resistance, and to raise a heat-conducting characteristic was tried, but. Since an effect is insufficient and also it cannot carry out industrially, it is hardly put in practical use until now. In order to color a stainless steel material or to improve the corrosion resistance, in painting, in order to raise the adhesion of a coat, the surface treatment by chemical conversion is usually performed before paint. As a surface treatment by such chemical conversion, although the conventional phosphate

process, a chromate process, etc. are generally performed, in these methods, preparation of a treating solution is complicated, and also there is a fault that the stable effect is not acquired.

[0006]

[Problem(s) to be Solved by the Invention]While promoting the distribution at the time of this invention being a basis of such a situation, improving the compatibility and the heat-conducting characteristic over a steam or a fluid to the surface of a stainless steel material, and contacting a fluid, and evaporation, It is made for the purpose of providing the surface treatment method of the stainless steel material for raising film adhesion.

[0007]

[Means for Solving the Problem]As a result of this invention person's repeating research wholeheartedly about a method of reforming the surface of a stainless steel material, a stainless steel material is immersed in iron oxide ion and an oxidation chromium-ions content treating solution which were prepared by specific processing, By making an iron oxide film form in that surface, it finds out that compatibility and heat-conducting characteristic over a steam or a fluid can be improved, and film adhesion may be improved, and came to complete this invention based on this knowledge.

[0008]To namely, iron oxide ion and an oxidation chromium-ions content treating solution which this invention uses a chromium iron alloy as the anode, and are produced by carrying out electrolytic treatment in an alkaline aqueous solution. A stainless steel material is immersed and a surface treatment method of a stainless steel material making an iron oxide film form in the surface is provided.

[0009]

[Embodiment of the Invention]In this invention method, the treating solution for making an iron oxide film form on the surface of a stainless steel material is prepared first. By carrying out electrolytic treatment in an alkaline aqueous solution by using a chromium iron alloy as the anode, this treating solution makes iron and chromium in an alloy eluted, and let it be an alkaline aqueous solution containing iron oxide ion ( $\text{FeO}_4^{2-}$ ) and oxidation chromium ions. Under the present circumstances, as a chromium iron alloy used as the anode, The ferritic stainless steel (SUS430, SUS405, SUS444, etc.) whose chromium content a carbon content is about 12 to 25 % of the weight at about 0.12 or less % of the weight, and a carbon content at about 0.10 to 1.00 % of the weight. An alloy with few nickel contents of the martensitic stainless steel (SUS410JI, SUS403, SUS410, etc.) etc. whose chromium content is about 11 to 17 % of the weight is preferred. the austenitic stainless steel (SUS304L.) of about 0.03 to 0.15 % of the weight of carbon contents, about 16 % of the weight or more of chromium content, and about 6 % of the weight or more of nickel contents The elution of the alloy with many nickel contents, such as SUS316L and SUS304, into iron and the alkaline aqueous solution of chromium does not take place easily (refer to drawing 1).

[0010]There is no restriction in particular about the cathode material used in this electrolytic treatment, the same thing as an anode material may be used, and other alkali-proof electrical conducting materials, for example, iron, titanium, a carbon material, etc. may be used. As an alkaline aqueous solution, what contains about 1-10 mol/l. of hydroxide of alkaline metals, such as sodium hydroxide, a potassium hydrate, and lithium hydroxide, for example is used. there is no restriction in particular about electrolytic treatment conditions -- for example, the degree of bath temperature of about 10-40 \*\* --

desirable -- 15-30 \*\* and about 50-200 mA of current -- desirable -- 70-150 mA and a for [ electrolysis time 10 to 300 minutes ] grade -- the galvanization is preferably carried out on condition of for 30 to 240 minutes.

[0011]The treating solution which iron and chromium are eluted in an alkaline aqueous solution from the alloy of the anode, and mainly contains iron oxide ion ( $\text{FeO}_4^{2-}$ ), and contains a little oxidation chromium ions by this electrolytic treatment is obtained. Although the iron oxide ion ( $\text{FeO}_4^{2-}$ ) concentration in this treating solution changes with a kind, electrolytic treatment conditions, etc. of an anode material, its range of 1000-3000 ppm is generally preferred.

[0012]A side reaction as this treating solution indicated to be with the passage of time by reaction-formula  $2\text{FeO}_4^{2-} + 2\text{CrO}_2^- + 2\text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3 + \text{CrO}_4^{2-} + \text{OH}^-$  occurs. Since there is a tendency for iron hydroxide to precipitate, when preparing a treating solution, it is desirable to present the surface treatment of a stainless steel material immediately. When precipitate of iron hydroxide arises by the above-mentioned reaction, it can return to the original state by adding an oxidizer like sodium hypochlorite to this, and performing same electrolytic treatment again.

[0013]Next, the stainless steel material which should be carried out a surface treatment is immersed, and an iron oxide film is made to form on the surface into the treating solution which was prepared by doing in this way and which mainly contains iron oxide ion ( $\text{FeO}_4^{2-}$ ), and contains a little oxidation chromium ions. There is no restriction in particular about the kind of stainless steel material to which such a surface treatment is made to perform, and both austenite, a ferrite series an austenite ferrite series a martensite system a precipitation-hardening system, etc. can be used. moreover -- as the processing condition in this case -- about 0-80 \*\* -- desirable -- for the temperature of the range of 20-60 \*\*, and 10 minutes -- or although for 30 minutes thru/or the processing time of about 3 hours are used preferably, restriction in particular does not have about 5 hours.

[0014]By such processing, the iron oxide ion ( $\text{FeO}_4^{2-}$ ) in a treating solution reacts to the stainless steel material surface chemically, and forms a stable firm  $\text{Fe}_2\text{O}_3$  (gamma- $\text{Fe}_2\text{O}_3$  is seemed) layer precisely.

[0015]Thus, the iron oxide film formed on the surface of the stainless steel material has compatibility to a steam or a fluid, raises heat-conducting characteristic and film adhesion, and also raises corrosion resistance further while promoting the distribution at the time of contacting a fluid, and evaporation.

[0016]

[Effect of the Invention]While promoting the distribution at the time of contacting a fluid, and evaporation on the surface of a stainless steel material according to the invention disposal method of this invention, heat-conducting characteristic and film adhesion are raised, and also the iron oxide film excellent in the compatibility over a steam or a fluid which also raises corrosion resistance can be made to form easily.

[0017]The stainless steel material by which the surface treatment was carried out by this invention method, From excelling in mass transfer and heat-conducting characteristic, for example Distillation, evaporation, absorption, Crystallization, gas conditioning, desiccation, an extracting apparatus and combustion, refrigeration facilities, etc. specifically A brewing fermentation device, A medicine manufacturing installation, a bio-related facility, etc. are useful for the use relevant to heat transfer and mass transfer, and since it excels in film adhesion, it is useful as stainless steel materials for paint, such

as the use as which the corrosion-resistant improvement and colorization by paint, and multiple color-ization are required, for example, building materials, a household appliance, vehicles, and a marine vessel. Since it excels in corrosion resistance, it is useful as corrosion-resistant building materials used under atmosphere, such as dust, a corrosive pulverization fluid, scattering salt water, a condensation nature gas and a steam, condensation, evaporativity exhaust gas.

[0018]

[Example]Next, an example explains this invention still in detail.

[0019]As a reference example chromium iron alloy, three sorts, SUS444 of ferritic stainless steel, SUS304L of austenitic stainless steel, and SUS316L, were used. Into 200 ml of solution of 6 mol/l. potassium hydrate concentration, the above-mentioned stainless steel (what has the same two poles) was immersed as the anode and the negative pole, by 24 \*\* of bath temperature, the voltage 1.999V was impressed, a direct current was sent at 100 mA, and electrolytic treatment was performed for 240 minutes. The iron oxide ion ( $\text{FeO}_4^{2-}$ ) concentration in a potassium hydroxide solution [ / in electrolytic treatment time 10 minutes, 20 minutes, 40 minutes, 80 minutes, 160 minutes, and 240 minutes ] was measured. About this result, SUS444, A and SUS304L, and B and SUS316L are shown in drawing 1 as C.

[0020]Drawing 1 is a graph which shows the relation between electrolytic treatment time and the  $\text{FeO}_4^{2-}$  concentration in KOH solution.

As for it, as this figure shows, SUS304L and SUS316L of austenitic stainless steel with many nickel contents turn out that iron in an alloy cannot be eluted easily.

[0021]Using SUS444 as the example 1 anode and the negative pole, electrolytic treatment was performed for 120 minutes like the reference example, and the treating solution containing iron oxide ion ( $\text{FeO}_4^{2-}$ ) 1000ppm was prepared. Next, using three sorts, SUS444, SUS304, and SUS316, as a stainless steel material which should be carried out a surface treatment, each was immersed into the above-mentioned treating solution, and the surface treatment was performed for 30 minutes at 40 \*\*.

[0022]Surface hydrophilicity was compared about the stainless steel material which performed the surface treatment, and the stainless steel material which was not given. Namely, JIS K6768 gets wet and index reference solution No.32 (surface tension 32 dyne/cm) and tap water (surface tension of about 72 dynes/cm) are used, About 0.02 ml was dropped on the surface of the stainless steel material, respectively, the average length of the major axis of the drop of 1 minute after and a minor axis was measured, and hydrophilic nature was compared. A result is shown in Table 1.

[0023]

[Table 1]

鋼 種	標準液 No. 32			水 道 水		
	未処理品 (a) (mm)	処理品 (b) (mm)	(b)/(a)	未処理品 (c) (mm)	処理品 (d) (mm)	(d)/(c)
SUS444	8. 0	≥21. 5	≥2. 7	7. 5	16. 0	2. 1
SUS304	8. 5	≥28. 0	≥3. 3	7. 0	7. 5	1. 1
SUS316	7. 5	≥29. 0	≥3. 9	8. 0	11. 5	1. 4

[Note] (a), (b), (c), and (d) show the average length of the major axis of a drop, and a minor axis.

[0024]As shown in Table 1, also in which steel type, the surface treatment article is excellent in hydrophilic nature compared with the unsettled article.

[0025]Using SUS444 as the example 2 anode and the negative pole, electrolytic treatment was performed for 120 minutes like the reference example, and the treating solution containing iron oxide ion ( $\text{FeO}_4^{2-}$ ) 3000ppm was prepared. Next, the stainless steel plate of SUS316L was immersed into the above-mentioned treating solution, and the surface treatment was performed for 30 minutes at 40 \*\*. About the unprocessed elegance for this surface treatment article and comparison, and the processing article by a chromate process, tens of angles of contact [ as opposed to water for each wettability ] were measured, and were compared. A result is shown in Table 2.

[0026]

[Table 2]

鋼材 (SUS316L)	接 触 角 (度)
無処理品	67
従来法処理品	9~23
本発明方法処理品	16~24

[0027]As shown in Table 2, while the processing article by this invention method is fully effective compared with unprocessed elegance and demonstrating equivalent performance as compared with the processing article by the conventional method, there is little dispersion in the numerical value of an angle of contact, and the stable wettability is shown.

[0028]The above-mentioned surface treatment stainless steel plate and the unprocessed stainless steel plate were applied to the vertical mold falling film evaporator, respectively, chilled water outlet temperature and refrigerating capacity were searched for, and heat-conducting characteristic was compared. The result is shown in drawing 2 as a graph which shows the relation between chilled water outlet temperature and refrigerating capacity. In drawing 2, a solid line is a processing article and a dashed line is an unsettled article. As for the surface treatment article, compared with unprocessed elegance, the rise of refrigerating capacity was clearly accepted so that drawing 2 might show. That is, it was checked by carrying out a surface treatment that heat-conducting characteristic improves.

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[Translation done.]